ORGANIC MASS SPECTROMETRY, VOL. 27, 763–764 (1992)



# OMS Letters



Dear Sir

## Differentiation among Isomeric Polyfunctional Nitroaromatics by Dimethyl Ether Chemical Ionization Mass Spectrometry in a Conventional Ion Source

Since aromatic positional isomers frequently cannot be reliably distinguished by their electron ionization (EI) or chemical ionization (CI) mass spectra, interest in new selective CI reagents has been widespread. Among the most recent and promising were nitric oxide using a Townsend discharge technique[1] and dimethyl ether (DME) in a quadrupole ion trap mass spectrometer (ITMS).[2,3] For a number of difunctional oxyaromatics in the ITMS, the adduct ions resulting from ion–molecule reactions with reagent-derived ions demonstrated both functional group and positional selectivity, whereas in a conventional ion source no structural selectivity was observed. The adduct ions observed were $[M + 1]^+$, $[M + 13]^+$, $[M + 15]^+$, $[M + 45]^+$ and $[M + 47]^+$ (proton, methine, methyl, methoxymethylene and protonated DME adducts).

We have examined the DME CI mass spectra of isomeric polysubstituted nitrobenzenes in a conventional ion source and have found that it is frequently possible to distinguish among positional isomers on the basis of the distribution of reagent-gas-derived adduct ions alone. Other adduct ions and a prominent fragment ion $[M - 16]^+$ may also aid in substantiating the assignments (Table 1). A Finnigan TSQ-70 ion source was operated at 80 °C and 3 Torr; other parameters were as described previously.[4] Use of this ion source at higher than 'normal' CI source pressures has also been described by others.[5] Samples (10–20 μg) were introduced by direct exposure desorption.[4]

In the simplest case, the DME CI mass spectrum of *o*-dinitrobenzene (1,2-DNB, Table 1, entry 1) was dramatically different from those of the *m* and *p* isomers (entries 2 and 3), which were essentially identical. For the *o* isomer the most abundant ion was $[M + 91]^+$ (protonated methoxymethylene dimer), and $[M + 61]^+$ (methyl DME) and $[M + 93]^+$ (protonated DME dimer) adduct ions were second in abundance; the fragment $[M - 16]^+$, which was the most abundant ion in the *m* and *p* cases, was unimportant.

In the cases of other di- and trinitroaromatics with nitro groups only at adjacent or *o* positions, the distribution of adduct ions was very similar to that of *o*-dinitrobenzene (Table 1). Examples were 2,3- and 3,4-dinitrotoluene (2,3- and 3,4-DNT, entries 4 and 5), 3,4-dinitrobenzyl alcohol (3,4-DNBAlc, entry 14), and 2,3,4- and 3,4,5-trinitrotoluene (2,3,4- and 3,4,5-TNT, entries 8 and 9). The lack of substantial abundances of the $[M + 15]^+$ adduct and the $[M - 16]^+$ fragment for any of these compounds was also consistent with observation for 1,2-DNB.

For 2,4- and 2,6-DNT (entries 6 and 7) the most abundant ion was the $[M - 16]^+$ fragment. These isomers were readily distinguishable by the low abundance of methyl adduct $[M + 15]^+$ and the absence of $[M + 17]^+$ adduct ions in the case of the 2,6 isomer. 2,4,6-TNT (entry 13) was distinguished by the presence of $[M + 15]^+$ as the most abundant adduct and the absence of other reagent-derived adduct ions. The three remaining TNT isomers (entries 10–12) represented various combinations of *o*, *m* and *p* nitro substituents and could readily be distinguished by comparison of abundances of the major adducts and the $[M - 16]^+$ fragment ion.

Table 2 shows that certain isomeric dinitrophenols also displayed significantly different DME CI mass spectra. For 2,4-dinitrophenol (2,4-DNP, entry 1) the two most abundant ions were, respectively, $[M + 30]^+$ and $[M - 16]^+$. The same two ions were also most abundant for the 6-methyl congener (2,4-DNMP, entry 5), but in the reverse order. For 2,6-DNP (entry 3) and its 4-methyl congener (2,6-DNMP, entry 4) the most abundant adduct ion was $[M + 91]^+$ and fragmentation to $[M - 16]^+$ was not extensive. Stable adduct ions were few for 2,5-DNP (entry 2), the only one of any consequence being $[M + 15]^+$.

The 2,4- and 2,6-dinitroanilines (2,4- and 2,6-DiNA) were also readily distinguishable on the basis of their DME CI adduct ions (Table 3, entries 1 and 2). The most abundant ions observed for the two isomers were $[M + 45]^+$ and

**Table 1. Dimethyl ether CI mass spectra of dinitrobenzenes and related compounds**

| Entry number | Compound[a] | Principal ions (% relative abundance) $[M - 16]^+$ | $[M + 16]^+$ | $[M + 17]^+$ | $[M + 29]^+$ | $[M + 30]^+$ | $[M + 61]^+$ | $[M + 91]^+$ | $[M + 93]^+$ |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 1,2-DNB | 5 | 2 | – | – | – | 25 | 100 | 22 |
| 2 | 1,3-DNB | 100 | 28 | 6 | – | – | – | 2 | – |
| 3 | 1,4-DNB | 100 | 34 | 9 | – | – | – | – | – |
| 4 | 2,3-DNT | 8 | 3 | – | – | – | 27 | 100 | 32 |
| 5 | 3,4-DNT | 7 | 2 | – | – | – | 29 | 100 | 34 |
| 6 | 2,4-DNT | 100 | 48 | 23 | 34 | – | 5 | 4 | – |
| 7 | 2,6-DNT | 100 | 9 | – | 23 | – | – | 3 | – |
| 8 | 2,3,4-TNT | 5 | 8 | – | – | – | 32 | 100 | 20 |
| 9 | 3,4,5-TNT | 4 | 5 | – | – | – | 39 | 100 | 23 |
| 10 | 2,4,5-TNT | 44 | 88 | – | 27 | – | 53 | 100 | 10 |
| 11 | 2,3,6-TNT | 67 | 100 | – | – | 10 | 42 | 78 | 10 |
| 12 | 2,3,5-TNT | 100 | 84 | – | 10 | – | 22 | 41 | – |
| 13 | 2,4,6-TNT | 34 | 100 | – | – | 10 | – | – | – |
| 14 | 3,4-DNBAlc | 2 | – | – | – | 39 | 100 | 25 | |
| 15 | 3,5-DNBAlc | 77 | 44 | 25 | – | 34 | 3 | – | |

[a] See text for definition of these abbreviations.

0030-493X/92/060763-02 $06.00




*Received 10 February 1992*
*Accepted 3 April 1992*

**Table 2. Dimethyl ether CI mass spectra of dinitrophenols**

| Entry number | Compound[a] | Principal ions (% relative abundance) [M − 16]⁺ | [M + 15]⁺ | [M + 30]⁺ | [M + 45]⁺ | [M + 47]⁺ | [M + 61]⁺ | [M + 91]⁺ |
|---|---|---|---|---|---|---|---|---|
| 1 | 2,4-DNP | 87 | 39 | 100 | – | 8 | 10 | 8 |
| 2 | 2,5-DNP | 21 | 23 | – | – | – | 3 | 2 |
| 3 | 2,6-DNP | 28 | 33 | 63 | – | 15 | 38 | 90 |
| 4 | 2,6-DNMP[b] | 15 | 21 | 44 | 12 | 35 | 50 | 100 |
| 5 | 2,4-DNMP[c] | 100 | 38 | 52 | 9 | 25 | 9 | 16 |

[a] See text for definition of these abbreviations.
[b] 2,6-Dinitro-4-methylphenol.
[c] 2,4-Dinitro-6-methylphenol.

**Table 3. Dimethyl ether CI mass spectra of nitroanilines and related compounds**

| Entry number | Compound[a] | Principal ions (% relative abundance) [M + 13]⁺ | [M + 15]⁺ | [M + 45]⁺ | [M + 47]⁺ | [M + 59]⁺ | [M + 61]⁺ | [M + 91]⁺ | [M + 93]⁺ |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 2,4-DiNA | – | 2 | 100 | 36 | 4 | 3 | 4 | – |
| 2 | 2,6-DiNA | 92 | 8 | 19 | 6 | 100 | – | 6 | – |
| 3 | 2-NA | 22 | – | 100 | 76 | 9 | 2 | 2 | 3 |
| 4 | 3-NA | 2 | 5 | 57 | 100 | 13 | 8 | 10 | 3 |
| 5 | 2M,3-NA[b] | 14 | 4 | 100 | 98 | 13 | 6 | 15 | 5 |
| 6 | 4M,3-NA[c] | – | 11 | 100 | 66 | 23 | 4 | 14 | 10 |
| 7 | 2M,5-NA[d] | – | 9 | 100 | 74 | 6 | 3 | 3 | 2 |

[a] See text for definition of these abbreviations.
[b] 2-Methyl-3-nitroaniline.
[c] 4-Methyl-3-nitroaniline.
[d] 2-Methyl-5-nitroaniline.

$[M + 59]^+$, respectively. In addition, the $[M + 13]^+$ adduct, which had been shown to result from $[M + (CH_2{=}OCH_3) - CH_3OH]^+$ in the ITMS studies,[2,3] was present in >90% relative abundance for 2,6-DiNA but was not observed for the 2,4 isomer.

While the majority of isomeric di- and trinitroaromatics reported here were readily differentiated, it is clear that the method failed for *m*- and *p*-dinitrobenzene and for 2,3- and 3,4-dinitrotoluene. In addition, the data for *o*- and *m*-nitroaniline (2- and 3-NA, entries 3 and 4, Table 3) showed only modest selectivity, and among the three methylnitroaniline isomers (entries 5, 6 and 7) the differences were even less significant. Thus the number of nitrosubstituents as well as their positions appears to play a role in the selectivity of ion–molecule reactions of DME with the aromatic substrate.

**Acknowledgement.** I am grateful to Dr T-H. Chen of the U.S. Army Armament, Research, Development and Engineering Center for generous gifts of the TNT isomers.

**Disclaimer.** The findings in this paper are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

*Yours*

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